

### **REMARKS/ARGUMENTS**

Reconsideration is respectfully requested of the Office Action of September 6, 2007, dated the same day as applicants' previous response. In accordance with MPEP Section 714.05, applicants' Supplemental Amendment of September 6, 2007, is considered prior in time to the Office Action of September 6, 2007.

The claims in the case are: Claims 1, 4 to 7, 11, 12 and 14 to 20.

It is noted that the provisional rejection of Claims 1, 7 and 8 on the ground of non-statutory obviousness type double-patenting in view of Claims 1 and 4 to 9 of the co-pending application 10/532,202 has been overcome by the terminal disclaimer filed June 7, 2007.

The rejection of Claims 1, 4, 7, 11, 12 and 14 to 16 under 35 U.S.C. § 102(b) as anticipated *Deller et al.*, U.S. 5,776,240, is traversed and reconsideration is respectfully requested. The *Deller* patent is assigned to the same assignee as the present application.

The express limitation found in Claim 1 of this application that the pyrogenically produced silica is "structurally modified" is not shown by *Deller*. No structurally modified silicas of any kind are described by *Deller*. Persons skilled in the art understand that a "structurally modified" silica is a silica that has been subjected to ball milling or equivalent means of structurally impacting the pyrogenically produced silica. This is noted on pg. 5,

beginning at line 23 of this application. The *Deller* patent shows granules of silica which have been prepared by dispersing silica in water, spray drying and then optionally heating and/or silanizing. See the Abstract. The particles typically have an average particle size of 10 to 120 microns and are used for catalyst supports, according to *Deller*. Among the silanizing agents are compounds such as those mentioned in the present application.

In the Advisory Action of June 27, 2007, the Examiner had said that applicants have not convincingly shown that the process of *Deller* actually works in a way that leads in a direction opposite to what is produced by applicants. Also, the Advisory Action challenged the fact that *Deller* intends to make larger particles from smaller ones which larger particles would then have a higher bulk density and can be used without producing significant dust. To support the facts as stated by applicants herein, there was filed on September 6, 2007, a second declaration by Dr. Meyer, co-inventor in this case. Dr. Meyer's C.V. is attached hereto.

Dr. Meyer explains on pg. 2 of his Second Declaration that applicants' process goes through the ball milling step to miniaturize the silica particles by destroying the aggregates of the primary particles. Dr. Meyer explains that *Deller* teaches away from the present invention because he makes larger particles from smaller ones. This represents essentially the reverse of what applicants do. It should be noted that Dr. Meyer is a co-inventor in the *Deller* patent and is, therefore, in a position to know and understand what is described in the *Deller* patent.

For a discussion of destructuring and how it comes about to produce a structurally modified metallic oxide filler which is distinctly different from a filler that has not been destructured, see *Nargiello, et al.*, U.S. 6,193,795, of record. See also U.S. 2002/0077388, U.S. 5,959,005 and U.S. 5,827,363, all of record, as well as the enclosed U.S. 7,144,930; Canadian 2,240,759 and WO/2004/089816, which are further evidence of the well-recognized meaning of structural modification in silica technology.

As Dr. Meyer points out in his Second Declaration, there is no disclosure of the structurally modified silicas in *Deller*. Neither is there any procedure described in *Deller* that would produce any structural modifications of the silica. The lack of any suggestion or disclosure of structural modification in *Deller* is clearly stated by Dr. Meyer. Applicants respectfully submit that *Deller* fails as a reference under 35 U.S.C. § 102(b) because *Deller* does not show each and every feature of the claimed invention which is required in order to sustain a rejection under 35 U.S.C. § 102(b).

Claim 1 specifies that the silica has been structurally modified by ball milling and possesses a DBP value at least 10% lower than a non-structurally modified silica.

Clearly, *Deller* does not anticipate the claimed invention.

Therefore, withdrawal of the rejection under 35 U.S.C. § 102(b) is respectfully requested.

The rejection of Claims 1, 4, 7 and 11 under 35 U.S.C. § 102(b) as anticipated by *Ettlinger et al.*, U.S. patent 5,665,156 is traversed and reconsideration is respectfully requested. *Ettlinger*, assigned to the same assignee as the present application, describes silanized, pyrogenically prepared silicas by spraying the silica first with water and then with a silane compound which typically has the formula  $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$  in which  $n$  is from 10 to 18 and  $\text{R}$  is alkyl. *Ettlinger* shows that these products are used as thickening agents in liquids, as agents for improving pourability and also as reinforcing agents. See col. 1, lines 9 and 10 as well as col. 3, lines 13 to 19. This thickening effect is based on the characteristic feature of the *Ettlinger* silica that it agglomerates to larger clusters due to its agglomerated structure having gaps in the clusters.

However, *Ettlinger* does not disclose structurally modified silicas and, more particularly, structurally modified silicas in lacquers. It is noted that *Ettlinger* is mentioned in applicants' international publication (WO 2004/020531) on pg. 1, lines 8 to 22 and on pg. 11, lines 4-5 as the European equivalent EP 0 672 731.

The difference between the silicas according to *Ettlinger* (U.S. 5,665,156) and the silicas according to the present invention is that the silicas according to the invention are structurally modified after the silanization. Dr. Meyer also confirms that *Ettlinger* does not disclose structurally modified silicas; see pg. 3, first para. of the Second Declaration of Dr. Meyer. It

should be noted that Dr. Meyer is also a co-inventor on the *Ettlinger* patent and, therefore, is in the best position to know what is disclosed and what is not disclosed in the *Ettlinger* patent.

From the example beginning on pg. 11 of applicants' specification (WO 2004/020531) one can see that the silica according to the invention shows no thickening effect but gives a good scratch resistance to lacquer coatings.

In the comparative examples shown in WO 2004/020531, silicas according to the *Ettlinger* are used.

From the Table 7 on pg. 17, one can see that the silica according to *Ettlinger* (comparative silicas 1 and 2) show a good thickening effect, but a low value for the scratch resistance. Dr. Meyer also confirms the thickening effect of the *Ettlinger* products; see pg. 3, second para. of Dr. Meyers' Second Declaration.

In contrast, the silicas according to the present invention show a low thickening effect, but a good result for the scratch resistance. This is also confirmed by Dr. Meyer on pg. 3, para. 3. The difference could not have been predicted.

Since *Ettlinger* fails to describe a structurally modified silica, the reference does not disclose each and every feature of the claimed invention.

Accordingly, the reference fails to anticipate the claims and, therefore, the rejection should be withdrawn.

The rejection of Claims 1, 4-7, 11, 12 and 14 to 20 under 35 U.S.C. § 103(a) in view of *Deller* or *Ettlinger*, both of record, taken with *Nargiello*, newly cited, U.S. 6,193,795, is traversed and reconsideration is respectfully requested.

Both *Deller* and *Ettlinger* are discussed above and the remarks apply here as well. Dr. Meyer has clearly stated that neither *Deller* nor *Ettlinger* disclose structurally modified silicas.

The Examiner notes that neither *Deller* nor *Ettlinger* disclose that the respective silanised pyrogenically produced silicas are “structurally modified”.

*Deller* ‘240 is concerned with and teaches how to obtain better supports for catalysts; see col. 1, lines 13-20 and 46-50. The granular products of *Deller* possess a clearly specified pore size profile, as shown in col. 4, lines 54, *et seq.*

*Ettlinger* ‘156 relates to making superior thickening agents in liquids including paints, resins, rubbers, cosmetics, toners, and as pourability enhancers and reinforcing fillers; see col. 3, line 13, *et seq.*

*Nargiello* discloses, in col. 6, lines 1-3, that her method pertains to destructuring of pyrogenic hydrophilic/hydrophobic metal oxides with certain physical-chemical properties that are used for a reinforcing filler in certain rubber compositions, in sealants, caulking compounds or adhesives. No filler is taught as being suitable for lacquer formulations, as for example defined in Claim 6 and Claim 17 herein.

In respect to the hydrophobizing agents, *Nargiello* refers to four U.S. patents (see col. 6, lines 23 to 28). These U.S. patents which disclose the hydrophobizing agents as follows:

U.S. 4,307,023 (*Ettlinger*) uses silicon oil, only (see col. 10, Claim 2). According to the present invention, no silicon oil is used or claimed.

U.S. 3,924,029 (*Schütte*) uses organohalosilane which is a mixture comprising monomethylchlorosilane, dimethylchlorosilane and trimethylchlorosilane (see col. 10, Claim 4).

According to the present invention these silanes do not fall within the scope of the claims.

U.S. 4,503,092 (*Klebe*) uses dimethyldichlorosilane only (see col. 4, Claim 2).

According to the present invention, this silane does not fall within the scope of the claims.

U.S. 4,326,852 (*Kratel*) does not disclose any hydrophobic silica at all.

Thus, *Nargiello* would not direct persons skilled in the art to use the silanes defined in applicants' claims herein.

Even if *Nargiello* were to be combined with the principal references the combination would not create *prima facie* obviousness of the subject matter claimed herein.

There is no reason presented in the record herein why a person skilled in the art would select the filler of *Nargiello* which has been treated with different silanes than the two that are defined by applicants' claims and replace the completely different fillers of *Deller* and *Ettlinger*.

The Official Action alleges on page 7 that it would have been obvious to "...modify the teachings of either *Deller, et al.* or *Ettlinger, et al.* by performing the additional dry milling process of *Naiziello, et al.* and thereby obtain Applicants' invention".

Applicants point out that the Office Action does not contain any explanation of why it would have been obvious to subject the materials of *Deller* or *Ettlinger* to "additional dry milling". There is nothing in *Nargiello* to suggest that the materials of *Deller* or *Ettlinger* would be improved in some specific way by subjecting those substances to additional dry milling.

*Deller* is concerned with establishing a certain pore size distribution. Additional milling would not appear to be consistent with the achievement of that goal. *Ettlinger* is concerned with a product having a desired thickening effect. Milling that product would not suggest that the described thickening effect would necessarily be maintained.

Applicants respectfully submit that the aims and goals of *Deller/Ettlinger* are quite focused on the methods described in those two patents whereby those aims and goals are achieved. To suggest that a person skilled in the art would go further and subject those substances of *Deller/Ettlinger* to a rigorous dry milling is not at all convincing and moreover, is lacking in any reasoned explanation to support that suggestion.

Attention is also invited to the evidence of record herein, going to the issue of unexpected results.



The application has ample data showing that the silanised, structurally modified, pyrogenically produced silicas defined by applicants' claims, when incorporated into lacquers, impart a substantial improvement in scratch resistance to the lacquered surface; see pg. 18, first para. The results are also shown in Table 8 on pg. 20 and are of special relevance to Claims 6, and 17-19. These beneficial results could not have been predicted from the combination of references.

First of all, neither *Deller* nor *Ettlinger* are directed to lacquer compositions and, therefore, if a person skilled in the art were interested in improving scratch resistance of lacquers, *Deller* and *Ettlinger* would not provide any useful information and would not be viewed as relevant prior art.

Secondly, even if *Nargiello*'s destructured silicas were to replace the silicas of *Deller* or *Ettlinger*, the result would not produce lacquer compositions because neither of the principal references disclose lacquer compositions.

Clearly, the lacquer compositions of Claims 6, 17 and 18 are not rendered *prima facie* obvious by the combination of references.

Favorable action at the Examiner's earliest convenience is respectfully requested.

Respectfully submitted,

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## **Curriculum vitae Dr. Jürgen Meyer**

Day of birth: September 25th., 1959

Place of birth: Würzburg/Germany

School education: 1965 - 1969 Volksschule Fuchstadt  
1969 - 1978 Röntgengymnasium Würzburg

Graduation: June 29th., 1978 baccalaureate

German Federal Armed Forces: July 1978 - June 1980

Study of chemistry: 1980 - 1986 - Chemie-Diplom at January 10th., 1986  
1986 - 1988 - Conferral of a doctorate,  
Examination for a doctorate at March 21th. 1988

Job: Start at May 1th. 1988 at Degussa as chemist in research and development, now  
director R & D Aerosil at EVONIK INDUSTRIES

Process for the production of metal oxide and metalloid  
oxide dispersions

The invention provides a process for the production of low-viscosity, highly filled dispersions of pyrogenic metal  
5 oxides and metalloid oxides.

Low-viscosity, highly filled dispersions of pyrogenic metal  
oxides or metalloid oxides are widely used. For example,  
silica and aluminium dioxide dispersions are used in  
polishing processes (chemical-mechanical polishing) or in  
10 the paper industry for the production of a paper coating.  
In the glass industry, highly filled silica dispersions or  
dispersions of silicon-titanium mixed oxide are used for  
the production of shaped glass articles.

US 5,116,535, US 5,246,624 and US 6,248,144 all describe  
15 processes for the production of low-viscosity dispersions  
of pyrogenic silicon dioxide powder (fumed silica).

Fumed silica powders are produced like other pyrogenic  
oxide powders, e.g. alumina or titanium dioxide, preferably  
by flame hydrolysis. In this process, a homogeneous mixture  
20 of a vaporous starting material of the subsequent oxide,  
e.g. silicon tetrachloride or aluminium chloride, is burnt  
with hydrogen, oxygen and an inert gas using a burner in a  
cooled combustion chamber. In a first step of this process,  
water is produced by the reaction of hydrogen and oxygen,  
25 and in a second step, this water hydrolyses the starting  
material with the formation of the pyrogenic oxide.

In this process, primary particles are initially formed,  
which can coalesce into aggregates as the reaction  
progresses. Aggregates here are primary particles that have  
30 fused together. The aggregates can cluster together further  
to form agglomerates. During the dispersing of pyrogenic  
oxide particles, even under the action of low dispersing  
energy, the agglomerates are first separated. With higher

dispersing energies, larger aggregates are also converted to small aggregates.

- The principle on which the documents US 5,116,535, US 5,246,624 and US 6,248,144 are based is the same, i.e. to achieve as complete as possible a destructuring of the fumed silica powder by the action of high shear energies. However, in order to be able to introduce the high shear energies into the system, this must have a high viscosity. The high viscosity is achieved in the production processes of the above documents by a high level of filling of silica powder, which has to be at least 40 wt.%, and preferably 50 to 60 wt.%. If the content of silica powder in these processes is reduced to values of less than 40 wt.%, the effectiveness of the dispersing is reduced to such an extent that only incomplete destructuring of the silica powder takes place and larger aggregates remain in dispersion. This can lead to sedimentation or gelation of the dispersion. The dispersion is then adjusted to the desired solids content by dilution.
- 20 A disadvantage of these processes is the time- and energy-intensive incorporation of the pyrogenically produced silica powder to achieve the required viscosity.

In addition, there is a process for the dispersion of pyrogenically produced metal oxides in an aqueous medium, in which two predispersed suspension streams under high pressure are depressurised via two nozzles. These nozzles have to be adjusted in such a way that the dispersion jets hit one another exactly and the particles grind one another as a result.

- 30 This process for the production of dispersions containing pyrogenically produced silica is described e.g. in EP-A-773270.

In this process, an aqueous predispersion is divided into two partial streams, which are brought together again under

high pressure. The particles grind one another during this process. In another embodiment, the predispersion is also placed under high pressure, but the collision of the particles takes place against armoured wall regions.

- 5 Dispersion can take place over the entire pH range, the alkaline range being preferred. If a dispersion with a high solids content in the acidic range is desired, it is advantageous to reduce the viscosity by means of suitable additives.
- 10 The precise adjustment of the two predispersed suspension streams is problematic in this process. Only with precise adjustment can uniform grinding of the silica powder take place. A further complicating factor is that, under the extreme stress on the nozzles at pressures of up to
- 15 3500 kg/cm<sup>2</sup>, these display marked wear, which has a negative effect on the above-mentioned adjustment and can lead to impurities entering the dispersion.

In the embodiment in which the collision of the particles takes place against armoured wall regions, it has been

20 shown that the wall regions are subject to marked wear and this embodiment is not suitable for the dispersing of fumed silica.

It is true of both high-pressure processes that the dimensions of the equipment available do not allow larger

25 quantities of dispersion to be produced inexpensively.

The object of the invention is to provide a process for the production of finely dispersed dispersions containing pyrogenically produced metal oxides as the solid phase, which avoids the disadvantages of the prior art. In

30 particular, it should be possible to incorporate pyrogenically produced metal oxides or metalloid oxides into an aqueous phase as rapidly as possible, the introduction of impurities should be minimal and it should be possible to implement the process economically.

The object is achieved by a process for the production of an aqueous dispersion of pyrogenically produced metal oxide or metalloid oxide powders with a BET surface area of between 5 and 600 m<sup>2</sup>/g, with a metal oxide or metalloid oxide content in the dispersion of between 5 and 25 wt.%, which comprises the following steps:

- water, which is optionally adjusted to pH values of between 2 and 4 by adding acids, is circulated from a receiving vessel via a rotor/stator machine, and
  - 10 - metal oxide powder or metalloid oxide powder is introduced, using a feed device, into the shear zone between the slots in the rotor teeth and the stator slots, continuously or discontinuously and with the rotor/stator machine running, in a
  - 15 - quantity such that a predispersion with a solids content of between 20 and 40 wt.% results, and, after all the metal oxide powder or metalloid oxide powder has been added,
  - the feed device closes and shearing continues in
  - 20 - such a way that the shear rate is in the range of between 10000 and 40000 s<sup>-1</sup>, and
  - then, by dilution, the predispersion is adjusted to the desired solids content of the dispersion while maintaining the dispersing conditions.
- 25 In a preferred embodiment, the shear rate can be between 20000 and 30000 s<sup>-1</sup>.

The process according to the invention can preferably be carried out with silica powder, alumina powder, doped silica powder, described e.g. in DE-A-19847161 or DE-A-10065028, or with silicon-aluminium mixed oxide powder, described e.g. in DE-A-4226711, DE-A-10135452, DE-A19919635 or US-A-2003/22081.

- Furthermore, in the process according to the invention, bases and/or acids may be added to the dispersion and/or predispersion. As bases, for example ammonia, ammonium hydroxide, tetramethylammonium hydroxide, primary, secondary or tertiary organic amines, sodium hydroxide solution or potassium hydroxide solution may be used. As acids, for example phosphoric acid, sulfuric acid, hydrochloric acid, nitric acid or carboxylic acids may be used.
- 10 Furthermore, in the process according to the invention, cationic polymers and/or aluminium salts may be added to the dispersion and/or predispersion. Suitable cationic polymers may be those with at least one quaternary ammonium group, a phosphonium group, an acid adduct of a primary, secondary or tertiary amine group, polyethylene imines, polydiallylamines or polyallylamines, polyvinylamines, dicyandiamide condensates, dicyandiamide-polyamine co-condensates or polyamide-formaldehyde condensates. Suitable aluminium salts may be aluminium chloride, aluminium hydroxychlorides of the general formula  $\text{Al}(\text{OH})_x\text{Cl}$  with  $x=2-8$ , aluminium chlorate, aluminium sulfate, aluminium nitrate, aluminium hydroxynitrates of the general formula  $\text{Al}(\text{OH})_x\text{NO}_3$  with  $x=2-8$ , aluminium acetate, alums such as aluminium potassium sulfate or aluminium ammonium sulfate, aluminium formates, aluminium lactate, aluminium oxide, aluminium hydroxide acetate, aluminium isopropylate, aluminium hydroxide, aluminium silicates and mixtures of the above compounds. The use of these aluminium compounds in the production of silica dispersions is already described in the German patent application with application number DE 10238463.0.
- 20  
25  
30

It can also be advantageous to add to the dispersion and/or predispersion a surface-active substances, which is of a non-ionic, cationic, anionic or amphoteric nature.



Finally, one or more preservatives can also be added to the process according to the invention. These can, for example, be compounds that are available under the trade names Preventol® from Bayer or Acticide® from Thor.

## 5 Examples

### Analytical determinations

Determination of the viscosity of the dispersions: the viscosity of the dispersions produced was determined using a rotary rheometer from Physica, model 300, and the CC 27  
10 measuring cup at 25°C. The viscosity value was determined at a shear rate of 10 s<sup>-1</sup> and 100 s<sup>-1</sup>.

Determination of the particle size present in the dispersion: the particle size present in the dispersion is determined by dynamic light scattering. The instrument used  
15 is the Zetasizer 3000 HSA (Malvern Instruments, UK). The median value of the volume distribution  $d_{50(V)}$  is given.

Determination of the shear rate: the shear rate in the process according to the invention is expressed as the peripheral speed divided by the distance between the  
20 surfaces.

The peripheral speeds can be calculated from the speed of the rotor and the rotor diameter. The distance between rotor and stator is approx. 1 mm in the dispersing devices used.

25 Dispersing devices used: the rotor/stator machines Conti-TDS 3 and Conti-TDS 4 from Ystral are used for dispersing.

Silica powders used: AEROSIL® 90 (approx. 90 m<sup>2</sup>/g), AEROSIL® 130 (approx. 130 m<sup>2</sup>/g), AEROSIL® 200 (approx. 200 m<sup>2</sup>/g) and AEROSIL® 300 (approx. 300 m<sup>2</sup>/g), all DEGUS  
30 AG, are used.

**Examples:** the pH of the predispersion can be between 2 and 4.5, as a result of the acidic nature of the pyrogenically produced silica and depending on the quality of the raw materials. If desired, the pH can be adjusted to be constant throughout the different silica batches by adding acid, e.g. aqueous hydrochloric acid, or base, e.g. aqueous ammonia solution, in order to achieve a constant grinding output.

During the grinding, a pH value of the predispersion close to the isoelectric point is advantageous, since the particles to be ground can be more readily ground in this case without having to overcome reciprocal electrostatic repelling forces. When alkaline pH values are being adjusted, it can be useful to pass through the area around pH 7 by rapid addition of the alkaline component.

In all the examples, a heating of the dispersion by the high energy input is countered by a heat exchanger, which limits the temperature increase to no more than 40°C.

**20 Examples 1-3: Production of acidic AEROSIL® 200 dispersions at a shear rate of approx. 20000 s<sup>-1</sup>**

32.5 kg of deionised water are initially charged into a 60 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 3 (stator slot: 4 mm ring and 1 mm ring, rotor/stator spacing approx. 1 mm) under shear conditions, the quantity of AEROSIL® 200 required for a predispersion of 13.0 wt.% (Example 1, comparative example), 24.0 wt.% (Example 2) and 28.5 wt.% (Example 3), corresponding to Table 1, is added.

Once the intake is complete, the suction nozzle is closed and shearing continues at 3000 rpm for a further 10 min. When the grinding is complete, deionised water is used to dilute to a concentration slightly higher than the desired

end concentration to be able to take into account the quantities of additives still to be added.

The pH is adjusted to 5.3 with ammonia solution. On reaching the desired pH, the remainder of the water needed is metered in to achieve the exact silica end concentration of the dispersion of 12 wt.%. Using the Conti TDS 3, homogenisation is performed for a few more minutes.

**Example 4: Production of an acidic AEROSIL® 200 dispersion at a shear rate of approx. 25000 s<sup>-1</sup>**

475 kg of deionised water are initially charged into a 1600 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 4 (stator slot: 6 mm ring and 1 mm ring, rotor/stator spacing approx. 1 mm) under shear conditions, 190 kg of AEROSIL® 200 are taken in. Once the intake is complete, the suction nozzle is closed and the 28.5 wt.% predispersion is sheared at 3000 rpm for a further 10 min. The pH of the predispersion is approx. pH 3.7. When the grinding is complete, deionised water is used to dilute to a concentration slightly higher than the desired end concentration of the dispersion of 12 wt.% to be able to take into account the quantities of additives still to be added.

The pH is adjusted to 5.0 with ammonia solution. More deionised water is used to adjust the concentration of the dispersion to 12 wt.% silica and, using the Conti TDS 4, homogenisation is performed for a few more minutes. The thorough mixing/homogenisation is additionally supported by a jetstream mixer from Ystral installed in the mixing tank.

**Example 5: Production of an alkaline AEROSIL® 300 dispersion at a shear rate of approx. 25000 s<sup>-1</sup>**

475 kg of deionised water are initially charged into a 1600 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 4 (stator slot:

6 mm ring and 1 mm ring, rotor/stator spacing approx. 1 mm) under shear conditions, 190 kg of AEROSIL® 300 (or a smaller quantity according to the Table) are taken in. Once the intake is complete, the suction nozzle is closed and  
5 the 28.5 wt.% predispersion is sheared at 3000 rpm for a further 10 min. The pH of the predispersion is approx. 3.6. When the grinding is complete, deionised water is used to dilute to a concentration slightly higher than the desired end concentration of 15% to be able to take into account  
10 the quantities of additives still to be added.

The pH is adjusted to 9.5 by rapidly adding ammonia solution. The thorough mixing/homogenisation is additionally supported by a jetstream mixer from Ystral installed in the mixing tank. On reaching the desired pH of  
15 9.5, more deionised water is used to adjust the concentration of the dispersion to 15 wt.% silica and, using the Conti TDS 4, homogenisation is performed for a few more minutes.

**Examples 6-15: Production of AEROSIL® dispersions starting from a predispersion of 35 wt.% and a shear rate of approx. 20000 s<sup>-1</sup>.**  
20

32.5 kg of deionised water are initially charged into a 60 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 3 (stator slot: 4 mm  
25 ring and 1 mm ring, rotor/stator spacing approx. 1 mm) under shear conditions, 17.5 kg of pyrogenically produced silica according to Table 1 are taken in.

Once the intake is complete, the suction nozzle is closed and the 35 wt.% predispersion is sheared at 3000 rpm for a  
30 further 10 min (Example 14: 30 min). When the grinding is complete, deionised water is used to dilute to a concentration slightly higher than the desired end concentration to be able to take into account the quantities of additives still to be added.

The pH is adjusted to the desired level using sodium hydroxide or ammonia solution. On reaching the desired pH, the remainder of the water needed is metered in to achieve the exact silica end concentration.

- 5 **Example 16: Production of an acidic AEROSIL® 200 dispersion starting from a predispersion with 21 wt.% in the presence of an aluminium salt**

- 43.5 kg of deionised water are initially charged into a 60 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 3 (stator slot: 4 mm ring and 1 mm ring) under shear conditions, 11.6 kg of AEROSIL® 200 are sucked in. Once the intake is complete, the suction nozzle is closed and the 21 wt.% predispersion is sheared at 3000 rpm for a further 10 min.
- 15 After the grinding, an aqueous aluminium chloride solution is added (10 wt.%, based on  $\text{Al}_2\text{O}_3$ ), so that, based on the quantity of AEROSIL® 200 used, a concentration of 0.01 mg  $\text{Al}_2\text{O}_3$  per  $\text{m}^2$  silica surface area is obtained. The pH of the dispersion is kept at a pH of between 3.8 and 4.5 by simultaneously adding 25 wt.% sodium hydroxide solution. After adding the required aluminium chloride solution, the pH is adjusted to 5.0 with the sodium hydroxide solution, the remainder of the deionised water needed is added to adjust the concentration of the dispersion to 20 wt.% and dispersing is continued for a further 5 minutes.
- 25

**Example 17: Production of an acidic AEROSIL® 200 dispersion starting from a predispersion with 35 wt.% in the presence of an aluminium salt**

- 35.75 kg of deionised water are initially charged into a 60 l stainless steel mixing tank. Then, with the aid of the suction tube of the Ystral Conti-TDS 3 (stator slot: 4 mm ring and 1 mm ring) under shear conditions, 19.25 kg of AEROSIL® 200 are sucked in. Once the intake is complete,
- 30

the suction nozzle is closed and the 35 wt.% predispersion is sheared at 3000 rpm for a further 10 min.

After the grinding, an aqueous aluminium chloride solution is added (10 wt.%, based on  $\text{Al}_2\text{O}_3$ ), so that, based on the  
5 quantity of AEROSIL® 200 used, a concentration of 0.01 mg  $\text{Al}_2\text{O}_3$  per  $\text{m}^2$  silica surface area is obtained. The pH of the dispersion is kept at a pH of between 3.8 and 4.5 by simultaneously adding 25% sodium hydroxide solution. After adding the required aluminium chloride solution, the pH is  
10 adjusted to 5.0 with the sodium hydroxide solution, the remainder of the deionised water needed is added to adjust the concentration of the dispersion to 20 wt.% and dispersing is continued for a further 5 minutes.

Examples 1, 2, 3 and 6 show the importance of a high  
15 filling level during grinding. A high filling level during grinding with a rotor/stator set leads to a reduction in the viscosity of the dispersion.

Examples 3, 4 and 6 show the importance of the shear rate for successful grinding. At a higher shear rate, even with  
20 a low concentration of the predispersion, an equivalent product, or even a product with a slightly lower viscosity, can be achieved.

Examples 10, 11 and 12 show that, with a higher concentration of the silica, a higher viscosity is  
25 obtained.

Examples 13, 14 and 15 show that, in addition to the shear rate and the filling level during grinding, the period of grinding and the pH of the predispersion also have an influence. A longer grinding period brings about a lower  
30 viscosity of the dispersion. A reduction from pH 4.4 to 3.5 brings about a marked reduction in viscosity for the same grinding period.

Examples 16 and 17 show that the addition of aluminium salts clearly reduces the viscosity of dispersions

containing silica. When the process according to the invention is applied with high shear rates, the viscosity of the dispersion can be reduced surprisingly markedly. This can be seen particularly clearly from Example 17.

Tab. 1: Dispersing parameters and physico-chemical data of the silica dispersions

Ex.	AEROSIL	Pre-dispersion wt. %	Pre-dispersion pH	Shear rate (approx.) s <sup>-1</sup>	Dispersion wt. %	Additive	pH	d <sub>50</sub> (v) nm	Visc. 10 s <sup>-1</sup> mPas	Visc. 100 s <sup>-1</sup> mPas
1	200	13.0	4.0	20000	12	NH <sub>4</sub> OH	5.3	130	1615	320
2	200	24.0	3.8	20000	12	NH <sub>4</sub> OH	5.3	130	50	32
3	200	28.5	3.7	20000	12	NH <sub>4</sub> OH	5.3	137	35	24
4	200	28.5	3.7	25000	12	NH <sub>4</sub> OH	5.0	128	9	8
5	300	28.5	3.6	25000	15	NH <sub>4</sub> OH	9.5	131	9	9
6	200	35.0	3.5	20000	12	NH <sub>4</sub> OH	5.3	104	12	11
7	200	35.0	3.5	20000	20	NaOH	10.0	81	40	35
8	200	35.0	3.5	20000	20	NH <sub>4</sub> OH	10.0	86	38	32
9	300	35.0	3.3	20000	22	NH <sub>4</sub> OH	10.3	91	70	53
10	90	35.0	4.0	20000	15	NH <sub>4</sub> OH	5.3	154	6	5
11	90	35.0	4.0	20000	20	NH <sub>4</sub> OH	5.3	155	26	15
12	90	35.0	4.0	20000	25	NH <sub>4</sub> OH	5.3	160	40	23
13	130	35.0	4.4	20000	15	NH <sub>4</sub> OH	5.3	165	39	20
14	130	35.0	4.4	20000	15	NH <sub>4</sub> OH	5.3	158	21	14
15	130	35.0	3.5*	20000	15	NH <sub>4</sub> OH	5.3	155	7	6
16	200	21.0	3.9	20000	20	NaOH, AlCl <sub>3</sub>	5.0	108	385	164
17	200	35.0	3.5	20000	20	NaOH, AlCl <sub>3</sub>	5.0	88	8	8

\* Predispersion adjusted to 3.5 with dilute HCl



**Claims:**

1. Process for the production of an aqueous dispersion of pyrogenically produced metal oxide and metalloid oxide powders with a BET surface area of between 5 and 600 m<sup>2</sup>/g, with a metal oxide or metalloid oxide content in the dispersion of between 5 and 25 wt.%, comprising the steps:
  - water, which is optionally adjusted to pH values of between 2 and 4 by adding acids, is circulated from a receiving vessel via a rotor/stator machine, and
  - metal oxide or metalloid oxide powder is introduced, using a feed device, into the shear zone between the slots in the rotor teeth and the stator slots, continuously or discontinuously and with the rotor/stator machine running, in a quantity such that a predispersion with a solids content of between 20 and 40 wt.% results, and, after all the metal oxide powder or metalloid oxide powder has been added,
  - the feed device closes and shearing continues in such a way that the shear rate is in the range of between 10000 and 40000 s<sup>-1</sup>, and
  - then, by dilution, the predispersion is adjusted to the desired solids content of the dispersion while maintaining the dispersing conditions.
2. Process according to claim 1, characterised in that the metal oxide or metalloid oxide powder is a silica powder, an alumina powder, a silica powder doped with alumina or a silicon-aluminium mixed oxide powder.

3. Process according to claims 1 or 2, characterised in that bases or acids are added to the dispersion and/or predispersion.
4. Process according to claims 1 to 3, characterised in that cationic polymers and/or aluminium salts are added to the dispersion and/or predispersion.
- 5 5. Process according to claims 1 to 4, characterised in that a surface-active substance is added to the dispersion and/or predispersion.
- 10 6. Process according to claims 1 to 5, characterised in that a preservative is added to the dispersion and/or predispersion.

## INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF THE SUBJECT MATTER		
IPC 7	C01B13/14	C01B33/141 C01B33/26 C01F7/02 G09G1/02
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C01B C01F G09G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/121156 A1 (LORTZ WOLFGANG ET AL) 5 September 2002 (2002-09-05) paragraph '0047!	1-3
A		4-6
A	US 2001/042493 A1 (GOLCHERT RAINER ET AL) 22 November 2001 (2001-11-22) paragraph '0010!	1-6
A	US 2002/134027 A1 (BATZ-SOHN CHRISTOPH ET AL) 26 September 2002 (2002-09-26) paragraphs '0026!, '0027!, '0033!, '0057!	1-6
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the International filing date *L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the International filing date but later than the priority date claimed *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family		
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ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PRODUCTION OF METAL OXIDE AND METALLOID OXIDE DISPERSIONS

(57) Abstract: Process for the production of an aqueous dispersion of pyrogenically produced metal oxide and metalloid oxide powders with a BET surface area of between 5 and 600 m<sup>2</sup>/g, with a metal oxide or metalloid oxide content in the dispersion of between 5 and 25 wt.%, comprising the following steps: - water, which is optionally adjusted to pH values of between 2 and 4 by adding acids, is circulated from a receiving vessel via a rotor/stator machine, and - metal oxide or metalloid oxide powder is introduced, using a feed device, into the shear zone between the slots in the rotor teeth and the stator slots, continuously or discontinuously and with the rotor/stator machine running, in a quantity such that a predispersion with a solids content of between 20 and 40 wt.% results, and, after all the metal oxide powder or metalloid oxide powder has been added, - the feed device closes and shearing continues in such a way that the shear rate is in the range of between 10000 and 40000 s<sup>-1</sup>, and - then, by dilution, the predispersion is adjusted to the desired solids content of the dispersion while maintaining the dispersing conditions.



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(12) **United States Patent**  
**Meyer et al.**(10) **Patent No.:** **US 7,144,930 B2**  
(45) **Date of Patent:** **\*Dec. 5, 2006**(54) **FUNCTIONALIZED, STRUCTURALLY MODIFIED SILICAS**(75) Inventors: **Jürgen Meyer, Stockstadt/Main (DE); Manfred Ettlinger, Karlstein (DE); Stephanie Frahn, Haibach (DE)**(73) Assignee: **Degussa AG, Düsseldorf (DE)**

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Canadian Application No. 2,359,530, Issued: Aug. 7, 2001.  
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(57)

**ABSTRACT**

Functionalized, structurally modified silicas with 3-methacryloxypropylsilyl and/or glycidyoxypropylsilyl groups on the surface are prepared by mixing the silicas with the silane and heat-treating, destructuring and grinding the mixture. The silicas are employed in radiation-curing coatings.

**6 Claims, No Drawings**

## FUNCTIONALIZED, STRUCTURALLY MODIFIED SILICAS

## INTRODUCTION AND BACKGROUND

The present invention relates to functionalized, structurally modified silicas, a process for their preparation and their use.

It is known to react silicon dioxide obtained by flame hydrolysis and with a surface area of 40 to 200 m<sup>2</sup>/g with 3-methacryloxypropyl-trimethoxysilane. The resulting silicon dioxide is then coated with a further shell of (meth)acrylate polymers and subsequently employed in dental compositions (EP 0 142 784 A1).

It is known to silanize a silica with hexamethyldisilazane and then to destructure or to compact it by mechanical effects (EP 0 808 880 A2).

The known silica has the disadvantage that it can be incorporated into coating systems only with difficulty or not at all because its thickening effect is too high.

It is therefore an object of the present invention to develop a functionalized, structurally modified silica which does not have this disadvantage.

## SUMMARY OF THE INVENTION

The above and other objects of the present invention can be achieved by functionalized, structurally modified silicas, characterized by functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidyloxypropylsilyl, with the following physico-chemical characteristic data:

BET surface area	m <sup>2</sup> /g	25-380
Particle size	nm	6-45
Tamped density	g/l	50-400
pH		3-10
Carbon content	%	0.1-15
DBP (dibutylphthalate) number	%	<200

The present invention also provides a process for the preparation of the functionalized, structurally modified silicas according to the invention, which is characterized in that

a silica is sprayed optionally first with water or dilute acid and then with a surface modification reagent or a mixture of several surface modification reagents in a suitable mixing vessel, with intensive mixing, the components are optionally re-mixed for 15 to 30 minutes and heat-treated at a temperature of 100 to 400° C. over a period of 1 to 6 h, and the functionalized silica is then destructured/compacted by mechanical effects and optionally re-ground in a mill.

According to the invention, a ball mill, for example, can be employed for the destructuring. The re-grinding can be carried out, for example, by means of an air jet mill or pinned disc mill.

A silica prepared pyrogenically by the route of flame hydrolysis of  $\text{SiCl}_4$  can preferably be employed as the silica. Such pyrogenic silicas are known from Ullmanns Enzyklopädie der technischen Chemie [Ullmanns Encyclopaedia of Industrial Chemistry], 4th edition, volume 21, page 464 (1982).

In a preferred embodiment of the invention, a pyrogenic silica with a surface area of approx. 200 m<sup>2</sup>/g can be reacted (Aerosil® 200).

Monomeric substances, such as the organo alkoxysilanes, e.g., 3-methacryloxypropyl-trialkoxysilane and/or glycidyl-oxypopyltrialkoxysilane, wherein alkoxy can be methoxy, ethoxy and/or propoxy, can be employed as the surface modification reagent.

The amount of silane can be metered in with respect to the silica such that no excess results. The excess silane can optionally be removed during the heat treatment.

The silica according to the invention can be employed in radiation-curing coatings containing a binder vehicle, for example UV coatings.

The scratch resistance of the surfaces is advantageously improved by the use of the silica according to the invention

The silicas according to the invention have only a slight influence on the rheology of the coating system. Because the viscosity of the coating is increased only slightly, relatively large amounts of silica can be incorporated into the coating.

The functional groups on the silica can react with organic compounds.

According to the invention, the pyrogenically prepared silicas according to table 1 can be employed as the silica for the silanization.

TABLE 1

[illegible]

TABLE 1-continued

Test method		Physico-chemical data of AEROSIL							
		AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX 50	AEROSIL TT 600
SiO <sub>2</sub> <sup>1)</sup>	%	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8
Al <sub>2</sub> O <sub>3</sub> <sup>2)</sup>	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	<0.05
Fe <sub>2</sub> O <sub>3</sub> <sup>3)</sup>	%	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.01	<0.003
TiO <sub>2</sub> <sup>4)</sup>	%	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
HCl <sup>5)</sup>	%	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Sieve residue <sup>6)</sup>	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.2	<0.05
(Möckler method, 45 µm)									
Drum size (net) <sup>11)</sup>	kg	10	10	10	10	10	10	10	10

<sup>1)</sup>in accordance with DIN 66131<sup>2)</sup>in accordance with DIN ISO 787/XI, JIS K 5101/18 (not sieved)<sup>3)</sup>in accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21<sup>4)</sup>in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23<sup>5)</sup>in accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24<sup>6)</sup>in accordance with DIN ISO 787/XVII, JIS K 5101/20<sup>7)</sup>based on the substance dried for 2 hours at 105° C.<sup>8)</sup>based on the substance ignited for 2 hours at 1000° C.<sup>9)</sup>special packaging protecting against moisture<sup>10)</sup>HCl content is a constituent of the loss on ignition<sup>11)</sup>V goods are supplied in sacks of 20 kg<sup>12)</sup>VV goods are currently supplied only from the Rheinfeiden works

1. in accordance with DIN 66131

2. in accordance with DIN ISO 787/XI, JIS K 5101/18 (not sieved)

3. in accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21

4. in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23

5. in accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24

6. in accordance with DIN ISO 787/XVII, JIS K 5101/20

7. based on the substance dried for 2 hours at 105° C.

8. based on the substance ignited for 2 hours at 1000° C.

9. special packaging protecting against moisture

10. HCl content is a constituent of the loss on ignition

11. V goods are supplied in sacks of 20 kg

12. VV goods are currently supplied only from the Rheinfeiden works

## EXAMPLE 1

Aerosil® 200 is mixed with 4 parts water and 18 parts 3-trimethoxysilyl-propyl methacrylate and the mixture is heat-treated at 140° C. under an inert gas. The silanized silica is then compacted to approx. 250 g/l on a continuously operating vertical ball mill. The silica obtained has the following properties:

BET [m <sup>2</sup> /g]	138
Tamped density [g/l]	242
pH	4.6
C content	5.7
Loss on drying [%]	0.6
Loss on ignition [%]	8.9
DBP number [%]	122

Experiments with AEROSIL R 8200 and Silica According to Example 1 in UV-Curing Binders:

## Experiment 1:

AEROSIL® is stirred into the binder 1 (ethoxylated pentaerythritoltriacyrylate) Sartomer SR 494, Cray Valley, with a dissolver and then predispersed for 5 min at 3000 rpm (disc Ø45 mm). The mixture is dispersed in a laboratory bead mill for 15 min (AEROSIL® 8200) or

20 min (silica according to example 1) at 2500 rpm and a pump output of 60% (AEROSIL® 8200) or 40% (silica according to example 1). 1 mm glass beads are used as the

beads. The dispersing quality is checked with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

3% photoinitiator is stirred into the coating. Application is carried out with the aid of a spiral doctor blade (amount applied 36 µm) on black-lacquered metal sheets. Curing is carried out with a UV unit (current uptake of the UV lamp (mercury vapour lamp) 7.5-10 mA, belt speed 10 m/min, irradiation intensity 1 W/cm).

## Experiment 2:

AEROSIL® is stirred into the binder 2 (epoxyacrylate) with a dissolver and then predispersed for 5 min at 3000 rpm (disc Ø 45 mm). The mixture is dispersed in a laboratory bead mill for 15 min at 2500 rpm and a pump output of 70% (AEROSIL® 8200) or 40% (silica according to example 1). 1 mm glass beads are used as the beads. The dispersing quality is checked with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

3% photoinitiator is stirred into the coating. Application is carried out with the aid of a spiral doctor blade (amount applied 36 µm) on black-lacquered metal sheets. Curing is carried out with a UV unit (current uptake of the UV lamp (mercury vapour lamp) 7.5-10 mA, belt speed 10 m/min, irradiation intensity 1 W/cm).

## Incorporation of Silica According to R 8200:

Marked foaming is already to be observed during the predispersing (10% AEROSIL® based on binder solids). The viscosity also increases sharply due to the AEROSIL® 8200 (see table 1). The foam is intensified during the dispersing in the bead mill. Application of the coating with a smooth, bubble-free surface is not possible.



Incorporation of Silica According to Example 1:

Slight foaming is to be observed during the predispersing (10% VP based on binder solids), the foam having disappeared after the bead mill dispersing. After application and crosslinking of the film, a smooth, high-gloss surface results.

Grindometer Values, Brookfield Viscosities:

TABLE 2

	Grindometer values, Brookfield viscosities:			
	Grindometer	Viscosity [mPa.s]		Pseudo-plasticity
	value [µm]	6 rpm	60 rpm	6/60
binder 1	—	160	158	1.0
binder 1 + Aerosil R 8200	<10	35,500	6,830	5.2
binder 1 + silica according to example 1	<10	451	389	1.1
binder 2	—	481	468	1.0
binder 2 + Aerosil R 8200	<10	53,300	10,600	5.3
binder 2 + silica according to example 1	<10	1,000	950	1.1

The metal sheets are scoured with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25%+45 g Sikron F500) with 100 strokes with the aid of a scouring and washing resistance testing machine (Erichsen). The shine before and 10 min after scouring is determined with a reflectometer (20° incident angle).

TABLE 3

	20° reflectometer value — Residual shine		
	before	after	[%]
binder 1	82.0	50.0	61.0
binder 1 + silica according to example 1	80.5	65.2	81.0
binder 2	89.6	46.5	51.9
binder 2 + silica according to example 1	87.8	67.4	76.8

Further variations and modifications of the foregoing will be apparent to those skilled in the art and are intended to be encompassed by the claims appended hereto.

European application EP 00 122 955.8 is relied on and incorporated herein by reference.

What is claimed is:

1. A functionalized, destructured silica, characterized by functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidylloxypropylsilyl, with the following physico-chemical characteristic data:

BET surface area	m <sup>2</sup> /g	25–380
Primary particle size	nm	6–45
Tamped density	g/l	50–400
pH		3–10
Carbon content	%	0.1–15
DBP number	%	<200

wherein said silica is produced pyrogenically by flame hydrolysis of SiCl<sub>4</sub> prior to surface modification.

2. The functionalized, destructured silica of claim 1 wherein the BET surface area ranges from 90±15 to 380±15.

3. A process for the preparation of functionalized, destructured silica having functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidylloxypropylsilyl, with the following physico-chemical characteristic data:

BET surface area	m <sup>2</sup> /g	25–380
Primary particle size	nm	6–45
Tamped density	g/l	50–400
pH		3–10
Carbon content	%	0.1–15
DBP number	%	<200

wherein said silica is produced pyrogenically by flame hydrolysis of SiCl<sub>4</sub> prior to surface modification,

comprising spraying silica first with water or dilute acid and then with a surface modification reagent or a mixture of several surface modification reagents in a mixing vessel, intensively mixing the silica and said reagent, optionally re-mixing the silica for 15 to 30 minutes and then heat-treating at a temperature of 100 to 400° C. over a period of 1 to 6 h, to thereby produce a functionalized silica, then destructuring or compacting said silica and optionally re-grinding said silica in a mill.

4. A coating composition containing the functionalized, destructured silica according to claim 1 in a binder vehicle.

5. A functionalized, structurally modified destructured silica, characterized by functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidylloxypropylsilyl, with the following physico-chemical characteristic data:

BET surface area	m <sup>2</sup> /g	25–380
Primary particle size	nm	6–45
Tamped density	g/l	50–400
pH		3–10
Carbon content	%	0.1–15
DBP number	%	<200

said functionalized, destructured silica being produced by spraying pyrogenically produced silica first with water or dilute acid and then with at least one of a surface modification reagent selected from the group consisting of 3-methacryloxypropylsilane, glycidylloxypropylsilane and mixtures thereof, in a mixing vessel, intensively mixing the silica and said reagent, optionally re-mixing the silica for 15 to 30 minutes and then heat-treating at a temperature of 100 to 400° C. over a period of 1 to 6 h, to thereby produce said functionalized silica.

6. The functionalized, destructured silica according to claim 5, which has been additionally subjected to destructuring or compacting and optionally re-grinding said silica in a mill.

\* \* \* \* \*

Original document

## MILLED SILICATES AND SILICAS USED IN INK JET PRINTING

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Applicant: DEGUSSA (DE)

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EP0876433 (B1

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### Abstract of CA2240759

A method for preparing precipitated silicates and silicas having good high shear rheology in high solid aqueous slurries. Destructuring of aluminum silicate and silica via dry milling results in decreasing DE oil absorption. The destructured materials are useful for ink jet coating formulations.

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**WO9722670**

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### MILLED SILICATES AND SILICAS USED IN INK JET PRINTING.

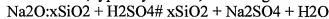
#### Introduction and Background

The present invention relates to low structure precipitated silicates and silicas and to a method of producing such low structure precipitated silicates and silicas. In a further aspect, the present invention also relates to a method for improving the rheology of precipitated silicates and silicas.

Yet another aspect of the present invention relates to ink jet coating compositions containing the destructured precipitated silicates and silicas as described herein.

Synthetic amorphous precipitated silicas and silicates have been used in the paper industry as both filler and coating pigments. Careful control of their properties allows them to be specifically engineered to meet the needs of the papermaker. This differentiates amorphous precipitated silicas and silicates from mineral pigments such as kaolin and ground  $\text{CaCO}_3$  which are mined and then processed.

Production of precipitated silica begins with the reaction of an alkaline sodium silicate solution with a mineral acid, typically  $\text{H}_2\text{SO}_4$ , according to the following equation:



In the case of synthetic silicates, a salt is used to acidify the sodium silicate solution. The reaction of alum with sodium silicate solution to produce a sodium aluminum silicate is as follows:  $4[\text{Na}_2\text{O} \cdot x\text{SiO}_2] + \text{Al}_2(\text{SO}_4)_3 \rightarrow \text{NaAl}_2\text{O}_3 \cdot 4[x\text{SiO}_2 \cdot 6\text{H}_2\text{O}] + 3\text{Na}_2\text{SO}_4$

In both precipitated silica and silicate manufacture, the two reactants are added simultaneously to water with agitation. The process parameters which significantly influence the properties of the pigments during the precipitation step include temperature, solids content, concentration and addition sequence of the reactants. During the precipitation step, small primary particles in the size range of 10-40 nanometers (100-400 Angstroms) aggregate via strong hydrogen bonds to form three dimensional aggregates. The maximum aggregate size formed during precipitation is < 1 micron. These aggregates, which are non-friable, are capable of withstanding the high capillary pressure that develops during drying.

Finally, the aggregates combine to form agglomerates in the size range of 0.4-5 microns. In contrast to the aggregates, agglomerates are friable with friability increasing with increasing size.

Following precipitation, the suspension containing the fully formed agglomerates is pumped to special filter presses which produce filter cakes at relative low solids content. Salts formed as byproducts during the precipitation process, predominately  $\text{Na}_2\text{SO}_4$ , are washed out at this point. Following filtration, the filter cake must be dried to remove as much water as possible. For paper applications, drying is followed by milling which reduces the size of agglomerates formed during the drying state.

The coalescence of primary particles to form aggregates, which then combine via strong hydrogen bond to form agglomerates, results in precipitated silica or silicate agglomerates which have internal void volume or porosity. As a result of this porosity, the measurement of surface area by the BET N<sub>2</sub> adsorption measurement method includes contributions from external, as well as internal, surface area of the agglomerate. The internal porosity or void volume is typically measured by oil absorption methods (e.g., dibutylphthalate (DBP)). The measurement of oil absorption (cc/100g) gives a direct indication of the degree of structure: very high (> 200), high (175-200), medium (125-175), low (75-125), and very low (75).

Synthetic amorphous precipitated silicas and silicates are low abrasion pigments. This is an important benefit to the papermaker since high abrasion in paper can result in accelerated wear on forming fabrics and slitter knives. Relative to kaolin clays, synthetic amorphous siliceous pigments are lower in abrasion than hydrous clays and are significantly lower in abrasion than calcined clays, paper grade talc and  $\text{TiO}_2$ . Another advantage is the ability of siliceous pigments to impart both brightness and opacity to paper. Precipitated amorphous silicate pigment as a filler in newsprint imparts a Tappi brightness similar to that of  $\text{TiO}_2$  and significantly greater than that of a low brightness calcined clay.

Aluminum silicates such as Degussa's P820 (Pasilex®; see Degussa Technical Bulletin Pigments No. 2, Degussa-Pigments for the Paper Industry) find numerous uses in the paper industry (e.g., for coatings to reduce strike through and show through in newsprint) and in emulsion and decorative paints to increase whiteness and hiding power (see Degussa Technical Bulletin Pigments No. 2).

### 34. Aluminum Silicate P820 for Emulsion and Decorative Paints).

Aluminum silicate P820 is currently supplied in the dry powder form which hinders its use in some applications, particularly in the paper industry, which is accustomed to receiving TiO<sub>2</sub> and minerals (e.g. kaolin and ground CaCO<sub>3</sub>) in slurry form. The low solids content (20-45%) that can be achieved with Pasilexe slurry adds considerably to its expense. However, increasing the solids content of Pasilexe results in higher viscosity slurries making the fluid incapable of being pumped by conventional equipment. The normal pumping viscosity for most conventional pumps is 3000-5000 cps with viscosities above this range requiring special displacement pumps.

U.S. Patent 5,261,956 shows that the rheological behavior of calcined clay slurries can be improved by destructuring the thermally structured mineral by milling.

For example, calcined clay slurries, typically shipped at 49% solids, can be increased to 56% solids by ballmilling prior to slurring. The resultant pigment when applied to paper as a coating shows only a slight decrease in sheet opacity due to the destructuring. However, calcined kaolin clays are very different materials in comparison to precipitated silicates and silicas.

### Summary of the invention

An object of the present invention is to provide destructured precipitated silicates and silicas and to be able to increase the solids content in aqueous slurries of precipitated silicates and silicas, or to reduce the viscosity of aqueous slurries while holding solids content unchanged.

In one embodiment of the invention, there is disclosed a method of producing low structure precipitated silicate or silica having good higher shear rheology in high solids aqueous slurries. The method involves dry milling precipitated silicate or silica in a media mill for a sufficient period of time to achieve approximately a 30-60% reduction in structure. In addition, there is disclosed a low structure precipitated silicate or silica produced by this method.

In another embodiment of the invention, there is disclosed a method of preparing a high solids aqueous slurry of low structure precipitated silicate or silica having improved fluidity. The method involves dry milling precipitated silicate or silica in a media mill for a sufficient period of time to achieve a 30-60% reduction in structure and forming a solids aqueous slurry. In addition, there is disclosed a high solids aqueous slurry of low structure precipitated silicate or silica produced by this method.

Still another embodiment of the invention relates to ink jet coating formulations based on the destructured precipitated silicas and silicates described above whereby higher solids contents can be obtained compared with standard ink jet coatings or lower viscosities can be obtained without changing solids content.

### Brief Description of the Drawings

The invention will be further understood with reference to the drawings, wherein:

Figure 1 is a graph showing the influence of milling time on DBP absorption in example 1 according to the invention;

Figure 2 is a graph showing the changes in DBP or (ADBP) over specific milling time intervals in example 1 according to the invention;

Figure 3 is a graph showing the changes in slurry viscosity when the solids content is held constant at 36.57% in example 1;

Figure 4 is a graph showing the influence of milling time on DBP absorption in example 2 according to the invention;

Figure 5 is a graph showing the Brookfield viscosity of P820 versus slurry solids level for milling times

0, 10, 20 and 30 minutes;;

Figure 6 is a graph showing the changes in DBP and surface area over specific milling time intervals in example 3 according to the invention;

Figure 7 is a graph showing the changes in DBP and solids content over specific milling time intervals in example 3 according to the invention;

Figure 8 is a graph showing the changes in viscosity and solids content over specific milling time intervals in example 3 according to the invention;

Figure 9 is a graph showing the particle size distribution curves for original FK500LS and various attrited versions of the FK-500LS in example 3 according to the invention;

Figure 10 is a plot of the zeta potential of siliceous pigments as a function of pH;

Figure 11 is a graph of brightness for various fillers; and

Figure 12 is a graph of opacity for various fillers.

#### Detailed Description of the Invention

In accordance with the present invention, a method is provided for the production of destructured precipitated silicates and silicas in order to increase the solids content in aqueous slurries of precipitated silicates and silicas. Precipitated silicates and silicas are dry milled in a media mill to produce the destructured precipitated silicates and silicas with increased particle size. No water is added to the milling process.

Milling the precipitated silicate or silica reduces the internal porosity as evidenced by a decrease in the DBP number. This results in a modification of the rheological properties of the slurry which increases its solids content without increasing viscosity.

The dry milling step is carried out in a media mill such as ball mills, attrition mills, and others known in the art. The media which can be utilized in the mill include 1/2 inch MgO stabilized Zirconia cylinders and others known in the art. Besides aluminum silicates such as Degussa's P820 (PasilexO), it is also possible to use other silica products such as Sipernate 50 and FK 500 LS, the latter especially suitable for use in ink jet coatings.

In accordance with a preferred aspect of the invention a precipitated silica known as FK500LS produced by Degussa was destructured via attritor milling. The milled product exhibits lower DBP numbers relative to the "as is" un-destructured material. Destructuring of the material allows the solids content of the silica in aqueous solution to be significantly increased with no increase in viscosity. Attritor milling of FK500 results in a precipitated silica particularly suitable for the coated ink jet paper market.

The accelerated growth in ink jet technology has placed greater constraints on the media, particularly in the area of four color printing. Silica coated papers are typically used for medium and high end color applications.

A suitable formulation for converters and paper makers uses a 80:20 blend of precipitated and fumed silica in conjunction with a binder such as PVA (polyvinyl alcohol).

The precipitated and fumed silica of choice are FK 310 and MOX 170, respectively, produced by Degussa.

The characteristics of FK 310 that make it applicable for ink jet media are an exceptionally high BET surface area of 650 m<sup>2</sup>/g and a moderate DBP oil absorption of 210. While FK 500LS can be a potential candidate for ink jet media, BET surface area of 450 m<sup>2</sup>/gram, its high DBP oil absorption of 330 is detrimental to paper coating applications. High oil absorption leads to high viscosity coating formulations and unacceptably high binder demands.

The following examples serve to illustrate the present invention.

#### Examples 1 and 2

Two separate tests were conducted which involved varying the amount of silicate charged into the test vessel, and the duration of milling. Physical characterization of the samples withdrawn from the ball mill at different times were conducted in order to better understand the morphological changes caused by the destructuring. Viscosity tests were conducted in the following manner: First, in Example 1, the solids level of the unmilled and destructured P820 slurries was kept constant and the Brookfield viscosity recorded using a Brookfield Viscometer. Second, in Example 2, the viscosity levels were kept constant and the solids content varied in order to match viscosities.

#### Sample Preparation

The mill used for performing the test was an

Attrition Mill, Model 1-S. The test tank used was lined with ceramic and the media used was 1/2" Steatite ceramic balls.

First, 140g of the silicate (250g for example 2) was poured into the test tank. The silica loading was 150 per batch and the rotational speed was set at 300 rpm. These values were selected based on past experience which showed optimum, or near optimum, destructuring capability for this mill.

Table 1 is a summary of changes in the physical characteristics of P820 due to ball milling for example

The loading level for the silicate was chosen using past experience. This silicate amount, while close to the optimum level for destructuring, did not supply enough of the much needed silicate for rheological testing. A second test run using more silicate with extended milling time was used to run viscosity test

Particle size has no real direct correlation with the amount of destructuring that occurs. The measured particle size, as measured by laser diffraction, actually increases due to the silicate being flattened during destructuring. The destructuring of the silicate reduces the internal porosity thereby decreasing the amount of liquid that can be absorbed allowing for higher slurry concentrations.

DBP absorption was determined using the

Brabender Plasti-Corder and surface area was determined using a Micromeritics Gemini surface area instrument using the established multipoint BET method. The DBP numbers, along with the ADBP, confirm that the absorptivity of the silicate steadily decreases with an increase in milling time. A direct correlation can be made between "internal" surface area and the decrease in absorptivity of the silicate. As milling continues the sponge like properties of the silicate are decreased through destructuring thereby decreasing absorptivity.

Figure 1 illustrates the decreasing absorptivity of the samples taken at different time intervals as milling proceeds during example 1. The plot of DBP vs.

milling time clearly shows the rate of destructuring for the aluminum silicate. Initially the rate is fast and then the curve starts to asymptote whereby destructuring efficiency decreases.

Figure 2 is a plot of change in DBP vs. milling time. The plot clearly shows the changes in DBP (ADBP) over specific time intervals. The change is initially rapid but over time the rate decreases.

Table 2 is a summary of the rheological properties of the aluminum silicate from example 1. For these series of tests the solids concentration was set at 36.6% and the Brookfield viscosity of the slurries were

determined as a function of milling time. The results indicate that milling significantly lowers slurry viscosity. For example, the viscosity data indicates that following 30 minutes of ballmilling, the viscosity of 36.6% slurry of P820 is decreased from 5280 to 66 cps. In addition, the slurry viscosity after 30 minutes of milling is essentially equivalent to that after 60 minutes, indicating that the degree of destructure needed to significantly decrease the slurry viscosity has been achieved within 30 minutes of ballmilling.

Figure 3 is a plot of DBP vs. viscosity when the solids content is held constant at 36.57%. A high DBP correlates with increased slurry viscosity.

Table 3 is a summary of changes in the physical characteristics of the aluminum silicate due to milling in example 2. In example 2, the silicate loading was increased to 250g in order to provide more product for rheological testing. The length of milling was increased in order to compensate for the extra silicate used. The observed trends closely parallel those observed in example 1. For example, particle size increases with increased milling time while DBP and internal surface area decrease with increased milling time. This is entirely consistent with the trends observed in example 1. However, the magnitude of the changes in DBP in example 2 is less than in example 1. This is most likely due to the larger amount of silicate used in example 2. Figure 2 (analogous to figure 1) clearly shows that the amount of destructure at a specific time in example 2 is less than that of example 1.

Figure 5 plots the Brookfield viscosity of P820 versus slurry solids level for milling times of 0, 10, 20, and 30 minutes. The unmilled P820 reached the 5000 cps range at 33% solids while the material ballmilled for 10 minutes allows the solids level to increase to 44% while maintaining a viscosity in the 5000 cps range. Following 20 minutes of milling the solids level can be increased to 47% while maintaining viscosity in the 5000 cps range.

Little additional benefit is observed by continued milling.

The unique physical properties of precipitated silica and silicate products, particularly their large internal void volumes and internal surface areas, allows destructure to be effectively achieved by ballmilling.

The destructure of aluminum silicate allows for significant increases in aqueous slurry solids while maintaining viscosities that are suitable for conventional pumps (i.e., 5000 cps). In the above examples, the aluminum silicate which was ballmilled for 20 minutes allowed the slurry solids to increase to a final solids of 47%, without significant increases in Brookfield viscosity. The above data suggests that significant transportation savings may be realized by ballmilling aluminum silicate prior to slurry makedown. This would be ideal for the paper industry which is accustomed to handling mineral pigments in slurry form. Specifically, to silicate (Pasilex 5) could be ballmilled and makedown at a central facility. shipped to newsprint plants where the advantages of structured silica and silicate pigments are well established. Of course, the reasons for using silicates such as Pasilex 01 i.e. reduction in strike through/side through, ink receptivity, and opacity, must not be significantly compromised by destructure of the material.

A further application of destructure silica and silicate materials may be in the paper coating area.

Oftentimes, the rheology of synthetic silicas and silicates constrains their use in conventional coating systems which typically use blade and rod coaters. The net result is that coating can only be done with these pigments at relative low solids levels. As shown above, the attainment of higher solids levels in aqueous slurries via destructure may allow for increased solids in coating formulations thereby facilitating use of silica pigments in specialty paper coating applications (i.e. ink jet paper).

#### Example 3

A precipitated silica (FK500LS) was destructure via attritor milling. The milled product exhibits lower

DBP numbers and BET surface areas relative to the original material. Destructuring of the material allows the solids content of the silica in aqueous solution to be significantly increased with no increase in viscosity.

The characteristics of the silicas described herein, such as FK 310, that make them applicable for ink jet media are an exceptionally high BET surface area ranging from about 400 to 700 m<sup>2</sup>/g.

Dry/milling results in decreased DBP oil absorption and internal surface area of the silica. This allows for significant increases in the solids content of the aqueous slurry with minimal increase in Brookfield viscosity.

The precipitated silica (FK500LS) was destructured by attrition milling to make it acceptable for ink jet paper coatings. The milling was performed using an Attrition Mill, Modell-S. The tank used was ceramic lined (A12O<sub>3</sub>), the media used was 1/4" Steatite ceramic balls and the shaft sleeves were Tungsten Carbide.

The shaft rotational speed was 300 rpm, the silica loading was 150g per batch. These final parameters were chosen using experience and from adjustments made from previous tests not listed.

**Rheological Tests** - The instrument used for assessing viscosity was a Brookfield Viscometer, Model RV using a No. 3 spindle rotating at 10 rpm. The various milled products were all dispersed in distilled water for testing. A 300 ml beaker was used as the test vessel.

First, 190 g of water was added to the beaker, and this was placed under a disperser with a cowles blade. Next, as water was being agitated by the blade, the silica was slowly added and the viscosity periodically checked until the desired consistency was achieved (25000 cps). The weight of the silica used was recorded and the solids content was calculated.

Table 5 displays most of the pertinent results of the testing performed. The values for DBP, particle size surface area, solids content and viscosity are listed. There are numerous interesting trends exhibited by the destructured silica. For example, the BET surface area and the DBP oil absorption decrease as milling time increases while the solids content necessary to reach the desired viscosity increases. The values obtained for the different categories, except viscosity, are either directly or inversely proportional.

Figure 6 is a graphical display showing both surface area and DBP. As stated earlier, the surface area and DBP oil absorption both decrease with increasing milling time. Surface area decreases linearly with milling time while the rate of decrease in DBP oil absorption, while initially rapid, appears to asymptote after 5 minutes. This trend can be shifted by making various modifications on the milling parameters but, eventually, DBP reduction will become less efficient as destructuring proceeds.

Figure 7 shows DBP and aqueous slurry solids content (4300-5500 CPS range) as a function of milling time. There is an inverse relationship exhibited between the two. As the DBP oil absorption decreases, the amount of silica required to reach the 4300-5500 cps viscosity range increases. For example, milling the silica for 7 minutes allows the silica solids content to increase from 13.8 to 24.1%, nearly double the solids level of the unmilled material.

Figure 8 is a plot of viscosity and solids content versus milling time. The curve that illustrates viscosity level was intentionally held in the 4800-5500 cps range. This plot serves to graphically illustrate the significant increases in solids levels which can be achieved by attritor milling.

Figure 9 shows the particle size distribution curves for original FK-500LS and various attrition milled versions of the FK-SOOLS. Examination of the original FK



SOOLS curve reveals the Gaussian or symmetrical nature of this air jet milled product. During air jet milling, the particle size is reduced, but the silica aggregates retain their overall original spherical shape. This type of milling allows a symmetrical and uniform size distribution to be obtained by laser particle size analysis. In contrast, the attritor milled silica exhibits an unsymmetrical particle size distribution and an increase in agglomerate size. These phenomena are caused by the mode in which the attritor mill operates. In attritor milling, the silica is milled by impingement of the material by the media. Since the silica is slightly malleable and porous, media impingement on the silica agglomerate flattens it, thereby periodically reducing the internal surface while consistently decreasing the external surface area (Tables 6). The flattened silica agglomerate particle, when analyzed by laser diffraction particle size analysis, appears to have increased in size since the laser views it in two dimensions. Figure 10 shows the zeta potential of siliceous pigments as a function of pH. Synthetic silicas and silica are anionic in the pH range 3.0 to 10.5 with the zero point of charge occurring at a pH of approximately

This is considerably lower than that of TiO<sub>2</sub> which has its isoelectric point at a pH of 5.0.

The lower isoelectric point of siliceous pigments has interesting consequences when used in conjunction with TiO<sub>2</sub> as fillers in acid papermaking systems. As the pH of TiO<sub>2</sub> is lowered from 9.5 to ca.

5.5, flocculation begins to occur. These soft flocs are readily dispersible in fiber. As the pH is lowered below the isoelectric point, denser flocculation occurs with a subsequent loss in dispersion and opacity power. Use of siliceous pigments prevents formation of dense TiO<sub>2</sub> agglomerates. The improved dispersibility allows 2:1 mixtures of TiO<sub>2</sub> and siliceous pigments to develop opacity similar to that of pure TiO<sub>2</sub>. This results in lower raw material costs to the papermaker.

Figure 11 shows that use of a precipitated amorphous silicate pigment as a filler in newsprint imparts a Tappi brightness similar to that of TiO<sub>2</sub> and significantly greater than that of a low brightness calcined clay.

As mentioned above, although siliceous pigments have a relatively low refractive index of 1.45, their structure results in solid/air interfaces which scatter light. The low bulk density of siliceous fillers, relative to more dense pigments, results in a greater number of particles and greater surface for light scatter at equal loading weights. Figure 12 shows that a synthetic amorphous silicate imparts greater opacity to newsprint at equal loading weights than either TiO<sub>2</sub> or calcined clay.

Three important criteria must be fulfilled for a precipitated silica to be used in coatings for ink jet paper:

1. The BET surface area of the silica should be as high as possible in order to maximize the ink receptivity of the coating.

2. DBP oil absorption should be moderate since high oil absorption results in increased viscosity of the coating and increased binder demand. DBP numbers for an ideal precipitated silica should be < 220 g/100 g silica.

3. The particle size of the silica should be small, preferentially in the 4Zm mean agglomerate size range.

FK 310, since it meets all the above criteria, has proven itself in numerous plant trials both in Europe and in North America. Attritor milled FK-50OLS, a high

BET surface area product, has value as a domestically produced precipitated silica for ink jet coatings since the decrease in DBP oil absorption upon destructuring allows it to meet the above criteria. In addition, a significant increase in coating solids offers advantages to the paper coater in terms of minimizing the rheological constraints that use of silica currently places on them.

Finally, if the silica agglomerates are indeed flattened by the attritor milling process, an increase in smoothness in the paper coating can result since the silica would more likely resemble the flat platelet structure of kaolin clay.

Table 6 shows the results of preparation of ink jet coatings with standard silicas and with destructured silicas.

For the preparation of ink jet coating formulations, polyvinyl acetate is dissolved in an equal amount of water at about 95°C. After that, the precipitated silica destructured as described herein is introduced with stirring at about 1000 rpm and subsequently dispersed therein at 3000 rpm.

Viscosity is measured (Brookfield) after the addition of the silica and also after one hour aging. For experiments in which the solids concentration was adjusted, i.e., undestructured silica experiments, the viscosity is adjusted at 100 rpm by diluting it with distilled water and stirring to 500 + 50 mPas. After one-half hour aging, the viscosity is then again adjusted at 100 rpm. Additionally, to check stability and shelf life, the viscosity of the ink jet coating formulation is tested after four days aging.

With untreated, non-destructured silicas (FK500LS and Supernat 50 S), it was not possible to prepare formulations with a solids content of 18% by weight. The ink prepared using standard FK-500LS could be dispersed when only half the amount of pigment is added.

The preparation had to be prepared with a spatula and was a dry paste. The product attempted to be made with the structured Supernat 50 S was gel-like and not dispersible.

Only with the addition of further water could dispersible preparation be formed, with resulting lower sol content of, for example, 12.7% and 9.6%.

The experiments done by Applicants has demonstrated that by using destructured precipitated silicas formed in accordance with the invention for silicas, such as Supernat 50 S and FK-500LS, it is possible produce ink jet formulation with a solids content of at least 18% by weight. Moreover, the destructured silicas of this invention exhibit less dust problems and can be more quickly incorporated into ink jet coating formulations. Also, they exhibit essentially no foaming problems when dispersed in conventional ink jet formulations.

In preparing the ink jet formulation, the usual pigments such as kaolin, calcium carbonate and vehicles such as PVA, starch, etc. can be used, as will be apparent to those skilled in the art.

It has also been found to be advantageous to mix a finely divided pyrogenically product silica such as Aerosil MOX 170 (Degussa) with the destructured silica for use in the ink jet formulation.

Further variations and modifications of the foregoing will be apparent to those skilled in the art, and such variations and modifications are intended to be encompassed by the claims that are appended hereto.

TABLE 1  
P-820 STRUCTURAL STABILITY  
ASSESSMENT OF MILLING ON LOADING CONCENTRATION  
Trial &#x2013;1  
EMI18.1

Surface <SEP> Surface

<tb> Moisture <SEP> Amt <SEP> of <SEP> Media <SEP> Drum <SEP> Test <SEP> Mean <SEP> Change <SEP> Area <SEP> Area  
 <tb> Sample <SEP> Content <SEP> Silicate <SEP> Loading <SEP> Rotation <SEP> Duration <SEP> Part. <SEP> DBP <SEP> IN <SEP> (m2), <SEP> (m2),  
 <tb> Designation <SEP> (%) <SEP> Used <SEP> (g) <SEP> (g) <SEP> (rpm) <SEP> (min.) <SEP> S <SEP> (um) <SEP> No.&num;, <SEP> DBP <SEP> (Internal) <SEP> (External)  
 <tb> P-820

<tb> Unmilled <SEP> 6.43 <SEP> 140 <SEP> 8007 <SEP> 63 <SEP> N/A <SEP> 8.36 <SEP> 205 <SEP> N/A <SEP> 11.53 <SEP> 64.18  
 <tb> P-820 <SEP> 6.43 <SEP> 140 <SEP> 8007 <SEP> 63 <SEP> 15 <SEP> 26.25 <SEP> 169 <SEP> 36 <SEP> 8.39 <SEP> 65.13  
 <tb> P-820 <SEP> 6.43 <SEP> 140 <SEP> 8007 <SEP> 63 <SEP> 30 <SEP> 26.72 <SEP> 149 <SEP> 56 <SEP> 8.66 <SEP> 64.93  
 <tb> P-820 <SEP> 6.43 <SEP> 140 <SEP> 8007 <SEP> 63 <SEP> 45 <SEP> 21.47 <SEP> 143 <SEP> 62 <SEP> 5.08 <SEP> 64.51  
 <tb> P-820 <SEP> 6.43 <SEP> 140 <SEP> 8007 <SEP> 63 <SEP> 60 <SEP> 21.57 <SEP> 134 <SEP> 71 <SEP> 3.55 <SEP> 64.29  
 <tb> TABLE 2

P-820 STRUCTURAL STABILITY  
 RHEOLOGICAL CHARACTERISTICS  
 Solids Content Kept &commat; 36.57%  
 Trial &num;1</RTI>  
 EMI19.1

Amt <SEP> of  
 <tb> Moisture <SEP> Amt <SEP> of <SEP> Water <SEP> Mixer <SEP> Mixing <SEP> Spindle <SEP> RTV <SEP> Actual  
 <tb> Content <SEP> Silicate <SEP> Used <SEP> Speed <SEP> Duration <SEP> Spindle <SEP> Spee <SEP> Raw <SEP> Viscosity  
 <tb> Sample  
 <tb> (%) <SEP> Used <SEP> (g) <SEP> (g) <SEP> (rpm) <SEP> (min) <SEP> No. <SEP> &num; <SEP> (rpm) <SEP> Data <SEP> (cps)  
 <tb> Designation  
 <tb> P-820 <SEP> 6.43 <SEP> 77 <SEP> 120 <SEP> 4000 <SEP> 15 <SEP> 5 <SEP> 50 <SEP> 66 <SEP> 5280  
 <tb> Unmilled  
 <tb> P-820 <SEP> 6.43 <SEP> 68 <SEP> 105 <SEP> 4000 <SEP> 4 <SEP> 2 <SEP> 100 <SEP> 16.4 <SEP> 66  
 <tb> Milled  
 <tb> 30 <SEP> min.  
 <tb>

P-820 <SEP> 6.43 <SEP> 67 <SEP> 105 <SEP> 4000 <SEP> 4 <SEP> 2 <SEP> 100 <SEP> 15.4 <SEP> 61.6  
 <tb> Milled  
 <tb> 60 <SEP> min.  
 <tb>

TABLE 3  
 P-820 STRUCTURAL STABILITY

## ASSESSMENT OF MILLING ON LOADING CONCENTRATION

Trial &amp;num;2

EMI20.1

Surface &lt;SEP&gt; Surface

&lt;tb&gt; Moisture &lt;SEP&gt; Amt &lt;SEP&gt; of &lt;SEP&gt; Media &lt;SEP&gt; Drum &lt;SEP&gt; Test &lt;SEP&gt; Mean &lt;SEP&gt; Change &lt;SEP&gt; Area &lt;SEP&gt; Area

&lt;tb&gt; Sample &lt;SEP&gt; Content &lt;SEP&gt; Silicate &lt;SEP&gt; Loading &lt;SEP&gt; Rotation &lt;SEP&gt; Duration &lt;SEP&gt; Part. &lt;SEP&gt; DBP &lt;SEP&gt; IN &lt;SEP&gt; (m2), &lt;SEP&gt; (m2),

&lt;tb&gt; Designation &lt;SEP&gt; (%) &lt;SEP&gt; Used &lt;SEP&gt; (g) &lt;SEP&gt; (g) &lt;SEP&gt; (rpm) &lt;SEP&gt; (min.) &lt;SEP&gt; S &lt;SEP&gt; (um) &lt;SEP&gt; No. &lt;SEP&gt; &amp;num; &lt;SEP&gt; DBP &lt;SEP&gt; (Internal) &lt;SEP&gt; (External)

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 250 &lt;SEP&gt; 8007 &lt;SEP&gt; 63 &lt;SEP&gt; 0 &lt;SEP&gt; 8.491 &lt;SEP&gt; 202 &lt;SEP&gt; 10.32 &lt;SEP&gt; 70.76

&lt;tb&gt; Unmilled

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 250 &lt;SEP&gt; 8007 &lt;SEP&gt; 63 &lt;SEP&gt; 30 &lt;SEP&gt; 28.59 &lt;SEP&gt; 167 &lt;SEP&gt; 35 &lt;SEP&gt; 8.67 &lt;SEP&gt; 72.41

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 250 &lt;SEP&gt; 8007 &lt;SEP&gt; 83 &lt;SEP&gt; 60 &lt;SEP&gt; 25.23 &lt;SEP&gt; 149 &lt;SEP&gt; 53 &lt;SEP&gt; 7.79 &lt;SEP&gt; 71.52

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 250 &lt;SEP&gt; 8007 &lt;SEP&gt; 63 &lt;SEP&gt; 120 &lt;SEP&gt; 59.53 &lt;SEP&gt; 139 &lt;SEP&gt; 63 &lt;SEP&gt; 5.92 &lt;SEP&gt; 73.64

&lt;tb&gt; TABLE 4

MILLED P-820

RHEOLOGICAL CHARACTERISTICS &amp;commat;VARIOUS SOLID LEVELS

Trial &amp;num;2&lt;/RTI&gt;

EMI21.1

Amt &lt;SEP&gt; of

&lt;tb&gt; Moisture &lt;SEP&gt; Amt &lt;SEP&gt; of &lt;SEP&gt; Water &lt;SEP&gt; Mixer &lt;SEP&gt; Solids &lt;SEP&gt; Mixing &lt;SEP&gt; Spindle &lt;SEP&gt; Actual

&lt;tb&gt; Sample &lt;SEP&gt; Content &lt;SEP&gt; Silicate &lt;SEP&gt; Used &lt;SEP&gt; Speed &lt;SEP&gt; Content &lt;SEP&gt; Durati &lt;SEP&gt; Spindle &lt;SEP&gt; Speed &lt;SEP&gt; RTV &lt;SEP&gt; Viscosity

&lt;tb&gt; Designation &lt;SEP&gt; (%) &lt;SEP&gt; Used &lt;SEP&gt; (g) &lt;SEP&gt; (g) &lt;SEP&gt; (rpm) &lt;SEP&gt; (%) &lt;SEP&gt; (mi &lt;SEP&gt; No. &lt;SEP&gt; &amp;num; &lt;SEP&gt; (rpm) &lt;SEP&gt; Raw &lt;SEP&gt; Data &lt;SEP&gt; (cps)

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 120 &lt;SEP&gt; 170 &lt;SEP&gt; 4000 &lt;SEP&gt; 38.36 &lt;SEP&gt; 15 &lt;SEP&gt; 5 &lt;SEP&gt; &lt;SEP&gt; 66 &lt;SEP&gt; 5280

&lt;tb&gt; Unmilled

&lt;tb&gt; P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 156.13 &lt;SEP&gt; 170 &lt;SEP&gt; 4000 &lt;SEP&gt; 44.38 &lt;SEP&gt; 13 &lt;SEP&gt; 5 &lt;SEP&gt; 50 &lt;SEP&gt; 48 &lt;SEP&gt; 3842

&lt;tb&gt; Milled

&lt;tb&gt; 30 &lt;SEP&gt; min.

&lt;tb&gt;

P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 161.4 &lt;SEP&gt; 170 &lt;SEP&gt; 4000 &lt;SEP&gt; 45.15 &lt;SEP&gt; 10 &lt;SEP&gt; 5 &lt;SEP&gt; 50 &lt;SEP&gt; 44 &lt;SEP&gt; 3520

&lt;tb&gt; Milled

&lt;tb&gt; 60 &lt;SEP&gt; min.

&lt;tb&gt;

P-820 &lt;SEP&gt; 7.30 &lt;SEP&gt; 194.39 &lt;SEP&gt; 170 &lt;SEP&gt; 4000 &lt;SEP&gt; 49.45 &lt;SEP&gt; 3 &lt;SEP&gt; 5 &lt;SEP&gt; 50

<SEP> 6 <SEP> 480  
 <tb> Milled  
 <tb> 60 <SEP> min.  
 <tb>

Table 5  
 MILLED FK-500LS  
 Properties and Characteristics  
 EMI22.1

Milling <SEP> time <SEP> Surface <SEP> Area <SEP> DBP <SEP> Mean <SEP> Particle <SEP>  
 Solids <SEP> Content <SEP> Actual <SEP> Viscosity  
 <tb> (min.) <SEP> (m<sup>2</sup>/g) <SEP> (g <SEP> oil/100g <SEP> silica) <SEP> Size <SEP> (um) <SEP> ('  
 <SEP> Reached <SEP> (cps)  
 <tb> 0 <SEP> 441.42 <SEP> 337 <SEP> 11.30 <SEP> 13.83 <SEP> 5000  
 <tb> 5 <SEP> 402.64 <SEP> 226 <SEP> 32.21 <SEP> 22.60 <SEP> 5500  
 <tb> 7 <SEP> 373.63 <SEP> 202 <SEP> 33.60 <SEP> 24.08 <SEP> 4800  
 <tb> 15 <SEP> 279.09 <SEP> 152 <SEP> 26.81 <SEP> 31.92 <SEP> 4300  
 <tb> Table 6  
 EMI23.1

Based <SEP> on <SEP> Based <SEP> on <SEP> Based <SEP> on <SEP> Based <SEP> on <SEP>  
 Based <SEP> on <SEP> Based <SEP> on <SEP> Based <SEP> on  
 <tb> FK <SEP> 310 <SEP> FK <SEP> 310 <SEP> FK <SEP> 500 <SEP> LS <SEP> FK <SEP> 500  
 <SEP> LS <SEP> FK <SEP> 500 <SEP> LS <SEP> Sipernat <SEP> 50S <SEP> Sipernat <SEP> 50S  
 <tb> Standard <SEP> Type <SEP> Standard <SEP> Type <SEP> Destructured <SEP> Destructured  
 <SEP> Standard <SEP> Type <SEP> Dastructured <SEP> Standard <SEP> Type  
 <tb> Formulation <SEP> &num; <SEP> 210 <SEP> 211 <SEP> 216 <SEP> 212 <SEP> 213 <SEP> 2  
 <SEP> 215  
 <tb> Components <SEP> (atro) <SEP> 30 <SEP> T <SEP> Mowiol <SEP> 30 <SEP> T <SEP> Mowi  
 <SEP> 30 <SEP> T <SEP> Mowiol <SEP> 30 <SEP> T <SEP> Mowiol <SEP> 30 <SEP> T <SEP>  
 Mowiol <SEP> 30 <SEP> T <SEP> Mowiol <SEP> 30 <SEP> T <SEP> Mowiol  
 <tb> 28-99 <SEP> (PVA) <SEP> 28-99 <SEP> (PVA) <SEP> 28-99 <SEP> (PVA) <SEP> 28-99 <SE  
 (PVA) <SEP> 28-99 <SEP> (PVA) <SEP> 28-99 <SEP> (PVA) <SEP> 28-99 <SEP> (PVA)  
 <tb> 80T <SEP> DBP <SEP> 254 <SEP> 80T <SEP> DBP <SEP> 254 <SEP> 80T <SEP> DBP <SEI  
 254 <SEP> 80T <SEP> DBP <SEP> 201 <SEP> 80T <SEP> DBP <SEP> 324 <SEP> 80T <SEP> DBI  
 <SEP> 200 <SEP> 80T <SEP> DBP <SEP> 322  
 <tb> 20 <SEP> T <SEP> MOX <SEP> 170 <SEP> 20 <SEP> T <SEP> MOX <SEP> 170  
 <tb> Solid <SEP> Content <SEP> (atro) <SEP> 18% <SEP> 18% <SEP> 18% <SEP> 18% <SEP> 18% <SEP>  
 18%/9.6% <SEP> 18% <SEP> 18%/12.7%  
 <tb> Viscosity <SEP> acc <SEP> to <SEP> Br.f.<SEP> (mPa <SEP> s) <SEP> (mPa <SEP> s) <SEP>  
 (mPa <SEP> s) <SEP> (mPa <SEP> s) <SEP> (mPa <SEP> s) <SEP> (mPa <SEP> s) <SEP> (mPa  
 <SEP> s)  
 <tb> --after <SEP> formulation  
 <tb> 5040 <SEP> 10560 <SEP> 960 <SEP> 4640 <SEP> 315200/12560 <SEP> 8820 <SEP> 80000/2  
 <tb> 5 <SEP> Upm <SEP> 3100 <SEP> 5720 <SEP> 820 <SEP> 2960 <SEP> 154000/6960 <SEP> 4  
 <SEP> 55600/1440  
 <tb> 10 <SEP> Upm <SEP> 1800 <SEP> 3190 <SEP> 620 <SEP> 1790 <SEP> 180000/3920 <SEP>  
 2720 <SEP> 52400/880

<tb> 20 <SEP> Upm <SEP> 948 <SEP> 1512 <SEP> 412 <SEP> 916 <SEP> > 80000/1680 <SEP> 13  
 <SEP> 30480/416  
 <tb> 50 <SEP> Upm <SEP> 604 <SEP> 892 <SEP> 316 <SEP> 586 <SEP> > 40000/916 <SEP> 786  
 <SEP> 15200/228  
 <tb> 100 <SEP> Upm  
 <tb> --after <SEP> 1 <SEP> h <SEP> 9000 <SEP> 11920 <SEP> 3600 <SEP> 11000 <SEP> ---/1368  
 <SEP> 9440 <SEP> ---/6220  
 <tb> 5 <SEP> Upm <SEP> 4720 <SEP> 6100 <SEP> 2280 <SEP> 5360 <SEP> ---/7160 <SEP> 3840  
 <SEP> --/3300  
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 <SEP> ---/1840  
 <tb> 20 <SEP> Upm <SEP> 1464 <SEP> 2100 <SEP> 898 <SEP> 1584 <SEP> ---/1592 <SEP> 1412  
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 --/564  
 <tb> 100 <SEP> Upm  
 <tb> --after <SEP> stirring <SEP> 3600 <SEP> 3320 <SEP> 460 <SEP> 2880 <SEP> ---/12400 <SEP>  
 3120 <SEP> --/4200  
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 ---/2640  
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 ---/736  
 <tb> 50 <SEP> Upm <SEP> 788 <SEP> 914 <SEP> 408 <SEP> 726 <SEP> --/780 <SEP> 712 <SEP>  
 /469  
 <tb> 100 <SEP> Upm  
 <tb> Viscosity <SEP> acc <SEP> to <SEP> Br.f <SEP> adjusted <SEP> to <SEP> 500 <SEP> #50  
 <SEP> mPa <SEP> s <SEP> by <SEP> diluting <SEP> with <SEP> water  
 <tb> --after <SEP> stirring  
 <tb> 100 <SEP> Upm <SEP> 458 <SEP> mPa <SEP> s <SEP> 462 <SEP> mPa <SEP> s <SEP> 396  
 <SEP> mPa <SEP> s <SEP> 400 <SEP> mPa <SEP> s <SEP> 488 <SEP> mPa <SEP> s <SEP> 472  
 <SEP> mPa <SEP> s <SEP> 438 <SEP> mPa <SEP> s  
 <tb> --after <SEP> ,5 <SEP> h/100 <SEP> Upm <SEP> 514 <SEP> mPa <SEP> s <SEP> 540 <SEP>  
 mPa <SEP> s <SEP> 456 <SEP> mPa <SEP> s <SEP> 452 <SEP> mPa <SEP> s <SEP> 505 <SEP> n  
 <SEP> s <SEP> 540 <SEP> mPa <SEP> s <SEP> 456 <SEP> mPa <SEP> s  
 <tb> --after <SEP> 4 <SEP> d/100 <SEP> Upm <SEP> 660/484\* <SEP> 662/494\* <SEP> 748/494\*  
 <SEP> 652/440\* <SEP> 830/594\* <SEP> 552/520\* <SEP> 570/526\*  
 <tb> Solid <SEP> content <SEP> (atro)  
 <tb> at <SEP> 500 <SEP> #50 <SEP> mPa <SEP> s <SEP> 17.2% <SEP> 16.9% <SEP> 17.9% <SEP>  
 17.1% <SEP> 9.0% <SEP> 17.3% <SEP> 12.6%  
 <tb> \*after 4 days and after stirring (100 Upm)

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Claims of CA2240759

Translate this text

We claim:

1. A method of making an ink jet coating formulation comprising dry milling a precipitated silicate or silica particulate in a media mill for a sufficient period of time to achieve a 30 to 60% reduction in structure as measured by the decrease in DBP number to form a dry milled product of reduced DBP number, dispersing said product into water to obtain aqueous slurry, and mixing said slurry with a binder for producing the desired ink jet coating.
2. The method according to claim 1 wherein said milling is carried out in a ball mill.
3. The method according to claim 1 wherein said milling is carried out in an attrition mill.
4. The method according to claim 1 wherein said mill contains as the media, MgO stabilized zirconia cylinders.
5. The method according to claim 3 wherein said mill contain spherical steatite ceramic attrition media.
6. The method according to claim 3 wherein the attrition mill is run at a shaft rotational speed of about 2 rpm.
7. The method according to claim 1 further comprising milling said silicate or silica particulate so that the media impinge on the said particulate to produce a milled particulate that exhibits an unsymmetrical particle size distribution and is agglomerated and is of decreased BET surface area.
8. An ink jet coating formulation comprising:
  - a) a binder vehicle for said formulation
  - b) a destructured silicate or silica having a DBP number that is 30 to 60% lower than the DBP number of un-structured silicate or silicas.
9. The ink jet coating formulation according to claim 8 which has a solids content of at least 18% by weight.
10. The ink jet coating formulation according to claim 8 wherein said binder vehicle is polyvinyl alcohol in an aqueous dispersion.
11. An ink jet coating formulation made by the method of claim 1.
12. A paper coated with the ink jet coating formulation of claim 8.

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For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PRODUCTION OF METAL OXIDE AND METALLOID OXIDE DISPERSIONS

(57) Abstract: Process for the production of an aqueous dispersion of pyrogenically produced metal oxide and metalloid oxide pow-  
ders with a BET surface area of between 5 and 600 m<sup>2</sup>/g, with a metal oxide or metalloid oxide content in the dispersion of between 5  
and 25 wt.%, comprising the following steps: - water, which is optionally adjusted to pH values of between 2 and 4 by adding acids,  
is circulated from a receiving vessel via a rotor/stator machine, and - metal oxide or metalloid oxide powder is introduced, using a  
feed device, into the shear zone between the slots in the rotor teeth and the stator slots, continuously or discontinuously and with the  
rotor/stator machine running, in a quantity such that a predispersion with a solids content of between 20 and 40 wt.% results, and,  
after all the metal oxide powder or metalloid oxide powder has been added, - the feed device closes and shearing continues in such  
a way that the shear rate is in the range of between 10000 and 40000 s<sup>-1</sup>, and - then, by dilution, the predispersion is adjusted to the  
desired solids content of the dispersion while maintaining the dispersing conditions.

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